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COMPLETE SPECIFICATION

Process for Carrying Out Chemical Reactions by means of a Ziegler Catalyst

We, STAMICARBON N.V., a Dutch Limited Liability Company of 2 van der Maesenstraat, Heerlen, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the performance of polymerization reactions in which a Ziegler catalyst is used.

By "Ziegler catalysts" is here to be understood catalysts formed by combining at least one compound of a metal of Groups 4a, 5a, 6a, 7a or 8 of the periodic system according to Mendelejeff, inclusive of thorium and uranium, or an organometallic compound of tin or lead with a metal, alloy, metal hydride, or organometallic compound of a metal of Groups 1 to 3 of such periodic system, whether or not in the presence of other substances, such as aluminium chloride.

In general it is relatively difficult to carry out a chemical reaction by means of a Ziegler catalyst on a technical scale in such a way that a product with constant properties is formed. For, the catalyst is particularly sensitive to traces of impurities, such as water and oxygen. In addition, the activity of the catalyst is influenced by the ratio in which the catalyst components are used, the time during which the catalyst components have previously been made to act on each other, and the temperature at which this action is effected. For instance, if ethylene is polymerized by means of a Ziegler catalyst, small changes in the said variables and in the concentrations of the said impurities have so great an influence that it is particularly difficult to make a polyethylene with a constant "melt index". The said changes, however, are usually so small that they cannot be detected during the polymerization process. Not until the product has been finished and the melt index of the product has been determined, can it be known whether or not disturbing changes have taken place.

The present invention is based on the surprising discovery that unpaired electrons exist in a liquid medium in which a Ziegler catalyst is present, such unpaired electrons belonging to the heavy metal atom. It is possible to measure the concentration of unpaired electrons in the liquid medium and if steps are taken to keep this concentration substantially constant during the course of the polymerization, it is found that this step materially promotes the formation of a polymeric reaction product of uniform properties.

The invention is applicable in continuous polymerization processes by keeping constant the concentration of unpaired electrons in the liquid medium in the polymerization zone. Alternatively, if the Ziegler catalyst is present in the liquid medium before this is fed to the polymerization zone, then the invention can be applied by keeping constant the concentration of unpaired electrons in the liquid before it enters the polymerization zone in addition to or instead of keeping the unpaired electron concentration constant in the polymerization zone itself.

Accordingly the present invention resides in a process of performing a polymerization reaction in an inert liquid medium by means of a Ziegler catalyst as herein defined wherein continuous or intermittent measurement is made either of the unpaired electron concentration obtaining in the liquid medium in the zone in which polymerization is taking place, or, in the event that the Ziegler catalyst is present in the liquid medium before this enters the polymerization zone, then of the unpaired electron concentration obtaining in the liquid medium in the polymerization zone and/or of the unpaired electron concentration

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obtaining in the liquid containing the catalyst before it enters the said zone, and wherein a said concentration or concentrations is or are corrected as necessary to maintain it or them substantially constant.

The unpaired electron concentration can be measured by passing a sample of the liquid containing the Ziegler catalyst through the resonance cavity of an electron spin resonance apparatus. A suitable design for such apparatus and a process for using it to measure unpaired electron concentration is described for instance in J. Smidt, Thesis Delft 1960, pages 19—40, E. H. Adema, c.s., Rec. trav. Chim. *80*, 173—180 (1961) or J. Smidt, Archives des Sciences *13*, 337—341 (1960).

It is preferable to apply the invention in a process in which the catalyst components are mixed with the liquid medium before this is fed to the polymerization zone so as to keep constant not only the concentration of unpaired electrons in the polymerization zone but also the concentration of unpaired electrons in the liquid containing the catalyst before this liquid enters the said zone. This offers the advantage that a distinction can be made between a change in the concentration of the unpaired electrons in the reactor caused by the preparation of the catalyst, and e.g. in the case that alkene is being polymerized, a change caused by the moisture content of the alkene passed into the reaction zone. The concentration of unpaired electrons in the reactor need not be the same as the concentration in the liquid containing Ziegler catalyst which is passed into the reactor. It need only be seen to that the two concentrations are maintained at appropriate values.

A favourable concentration of the unpaired electrons for obtaining the polymer properties desired can be established by a few preliminary tests. In the polymerization of substances containing terminal double carbon-carbon bonds, it has been found that the polymer produced has better mechanical properties according as the concentration of unpaired electrons in the liquid medium is lower.

In general the measurement can be carried out at the temperature of the liquid containing Ziegler catalyst or of the contents of the reactor, so that it is not necessary to cool or heat a sample before the determination.

The changes in the concentration of unpaired electrons can in principle be made to operate a warning device indicating the need for manual adjustment of the process or to initiate an automatic control of the chemical reaction. For instance, in the continuous polymerization of ethylene the ratio between the catalyst components can be automatically controlled in such a way that the measured concentration of unpaired electrons remains at a desired value.

The following examples illustrate the phenomenon of varying electron concentration and show ways in which it may be controlled.

Example 1

At room temperature 50 ml of a solution of $TiCl_4$ in heptane (0.10 mole/litre) and 2 ml of a solution of diethyl aluminium chloride in heptane (1.25 moles/l) are passed into a glass vessel under nitrogen. To the vessel a circulation conduit is connected which passes through the resonance cavity of an electron spin resonance apparatus. The concentration of unpaired electrons that can be measured by means of this apparatus has become constant after 5 minutes, when it amounts to 0.20 mmole/litre.

After 60 minutes ethylene is passed into the vessel as a result of which a powdery polymer is formed. The change in the concentration of unpaired electrons depends on the rate at which ethylene is supplied, the concentration of unpaired electrons being higher at a low supply rate than it is at a high supply rate. This effect is illustrated in Table 1. The polymerization time for these experiments is also 60 minutes.

Table 1

ethylene supply (litre/hour)	concentration of unpaired electrons during the polymerization (mmoles/litre)
1.6	0.53
9.0	0.22

EXAMPLE 2

To the catalyst solution described in example 1 the amounts of water mentioned in table 2 are added by replacing the dry nitrogen over the solution by wet nitrogen. The concentration of unpaired electrons appears to rise at first. If more than 0.2 mmole of water is added, the said concentration subsequently drops again.

TABLE 2

water (mmole)	concentration of unpaired electrons (mmole/litre)
—	0.20
0.1	0.43
0.2	0.58
0.25	0.54
0.50	0.43
0.75	0.29
1.00	0.24
1.25	0.16
1.50	0.05
1.75	0.03
2.00	0.01

EXAMPLE 3

Addition of a solution of ethanol in heptane (0.66 gmole/l) to the catalyst solution described in example 1 makes the concentration of unpaired electrons decrease as is shown in table 3.

TABLE 3

ethanol (mmole)	concentration of unpaired electrons (mmole/litre)
—	0.20
0.053	0.19
0.112	0.17
0.31	0.16
0.64	0.11
1.08	0.06
1.72	0.02
2.4	0.01

EXAMPLE 4

Addition of a solution of carbon tetrabromide in heptane (0.64 gmole/l) to the catalyst solution described in example 1 makes the concentration of unpaired electrons decrease as indicated in table 4.

TABLE 4

carbon tetrabromide (mmole)	concentration of unpaired electrons (mmole/litre)
—	0.20
0.12	0.17
0.35	0.12
0.54	0.10
0.77	0.085
1.28	0.060
1.92	0.042
2.52	0.030
2.85	0.024

EXAMPLE 5

Oxygen is added in the way water was added as described in example 2 by replacing part of the nitrogen by the calculated amount of dry air. As more oxygen is added the concentration of unpaired electrons first rises and then falls again. After addition of about 1.2 mmoles of oxygen this concentration is zero.

The phenomena described in the examples also occur at appreciably lower catalyst concentrations (e.g. 1—10 mmoles of the catalyst components per litre), and also if other Ziegler catalyst components are used, e.g. di-isobutyl aluminium chloride, di-isobutyl aluminium hydride, methyl aluminium dichloride, dimethyl aluminium chloride, or cyclopentadienyl titanium dichloride.

WHAT WE CLAIM IS:—

1. A process of performing a polymerization reaction in an inert liquid medium by means of a Ziegler catalyst as herein defined, wherein continuous or intermittent measurement is made either of the unpaired electron concentration obtaining in the liquid medium in the zone in which polymerization is taking place, or, in the event that the Ziegler catalyst is present in the liquid medium before this enters the polymerization zone, then of the unpaired electron concentration obtaining in the liquid medium in the polymerization zone and/or of the unpaired electron concentration obtaining in the liquid containing the catalyst before it enters the said zone, and wherein a said concentration or concentrations is or are corrected as necessary to maintain it or them substantially constant.

2. A process according to Claim 1, applied to the polymerization of a substance or substances containing terminal double carbon-carbon bonds.

3. A process according to Claim 1, applied to the polymerization of ethylene.

4. A polymeric material prepared by a polymerization process according to any preceding claim.

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